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Reliability conditions of Eh measurements in lake sediments

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**Published by the
COMMISSION OF THE EUROPEAN COMMUNITIES
Directorate-General
'Scientific and Technical Information and Information Management'
Bâtiment Jean Monnet
LUXEMBOURG**

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A bibliographical slip can be found at the end of this volume

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Printed in Belgium

ISBN 92-825-0681-9

Catalogue number : CD-NO-78-017-EN-C

INTRODUCTION

Lake sediments are very complex entities. They contain widely varying proportions of organic matter which are commonly correlated in magnitude with the intensity of biological production or of organic pollution of the overlaying waters. The organic fraction of the sediment is continuously broken down by bottom living organisms and as a result fresh organic material is continuously being added to the sediment surface. These demolition activities demand oxygen. Therefore, the sediment acts as a sink for that gas which must be supplied through the sediment surface at a rate governed by three factors: a biological oxygen demand arising from respiration and metabolic activities in the sediment, a chemical oxygen demand arising from the fact that such inorganic elements as Fe^{++} released into the sediment from decomposing biological structures accumulate in reduced form, and diffusion which regulates the transport.

During the autumnal and winter circulation the oxygen supplied from the atmosphere and produced by photosynthesis is continuously delivered by turbulent water movements to the sediment surface. During the summer stratification, however, the sediment is cut off from the oxygen supply. In the first case the oxygen concentration never falls to zero at the interface, and oxygen is present in the upper part of the sediments. In the second case the oxygen concentration falls to analytical zero even in the water layers immediately above the interface. It is evident from the above considerations that the oxidation conditions in the vicinity of the water-sediment interface is a critical factor regulating the chemical exchange between sediment and water [1, 2, 3].

This, in itself, seems to justify monitoring the environmental oxidation state, even if some authors [4, 5] have raised some objections concerning the general validity of the above formulation; Whitfield [6], however, emphasized the possibility of using the parameter defining the oxidation conditions of an aquatic environment for operational purposes.

This parameter is the redox potential, E_h , defined by the chemical potential of the electrons, considered as a chemical species taking part in every electrochemical exchange process. From this definition follows its nature as an overall quantity, determining, at any given temperature, the ratio of the thermodynamic activities of the components participating in any individual redox equilibrium. Since the activity is a single-valued function of the concentration, at any defined redox potential, a well determined concentration ratio of each species taking part in any individual equilibrium is defined.

We recalled this thermodynamic meaning of the redox potential since the fundamental law of equilibrium in the polyphasic system also applies for the electron species; it states that the chemical potential of every

single component is equal in every phase of a heterogeneous system in thermodynamic equilibrium. Sometimes, when measuring the redox potential, such a fundamental condition is not complied with as far as the phase "electrode" is concerned. Furthermore, in the presence of an additional phase, as happens in the case of E_h measurements in the sediments, the situation becomes yet more complex when the particles constituting the sedimentary phase undergo irreversible chemical transformations determining diffusion processes of the resulting species towards the electrode surface.

The causes of errors to be aware of in the E_h measurements into the sediment layers may be grouped in three categories.

The first involves the alterations of the electrode surface due to chemical reactions between the electrode material and the dissolved chemical species. The second is due to electrode polarization as a consequence of a current flow during the measurements. The third category involves the phenomena connected with a transient alteration in the morphologic distribution of the sedimentary layer due to the sampling procedure and electrode introduction. This operation induces an unavoidable alteration of the oxygenation conditions at the top of the column containing the mud sample with respect to the quasi stationary natural conditions.

We proceed to examine point by point the nature and the peculiarities of these perturbations in order to draw some conclusions about the evaluation of the actual reliability of the E_h measurements.

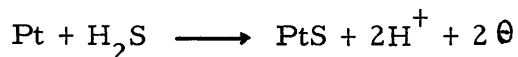
Electrode Surface Alterations

In order to behave as a pure redox electrode it must be completely inert, i. e. serve only to transfer electrons from the reduced to the oxidized species.

Whitfield [7] examined the behaviour of platinum from the point of view of the possibility of formation of surface compounds and tabulated the values of the normal potentials corresponding to the standard free energy of formation of various possible compounds.

The subject, however, is not so simple and cannot be considered only in terms of the thermodynamic stability of the bulk compounds. Contrary to the sp metals having complete d orbitals, the adsorption processes onto the surface of the so-called transition group metals involve medium-high energies, (a fact which explains their catalytic properties). The phenomenon has been studied by among others, Conway and Bockris [8], by Vijk [9] and extensively by Trasatti [10] as far as the hydrogen evolution reaction is concerned.

The reaction of H_2S on platinum, which is recognized as an important cause of platinum surface alteration in some anaerobic environments [11] has been studied by IJzermans [12]. He found for the electromotive force for the H_2S saturated 25°C isotherm a pH dependence of 59 mV. The curve, extrapolated at pH=0 yields a value of 221 mV vs. NHE which agrees fairly well with the process



if the values of the standard molar free enthalpies of formation of H_2S and PtS as given by Smithells [13] are taken.

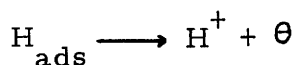
On the other hand, the abnormal slope of 40 mV in the e.m.f. vs. the logarithm of the H_2S equilibrium partial pressure may be explained only in terms of chemi-sorbed atomic hydrogen concentration following the Freundlich law:

$$c_{\text{H}} = k \cdot p_{\text{H}_2\text{S}}^n$$

with an n-value of 0.68.

The capability of platinum to break hydrogen-containing molecules, giving a strong chemisorption bond, is not surprising as it has also been demonstrated for many organic substances such as gliossal [14] and other compounds [15, 16]. The kinetics of such processes, as well as the concentration, depend also on the nature of the substance which determines whether the adsorption is diffusion-controlled ($t^{1/2}$ dependence of the coverage factor θ) or activation-controlled ($\ln t$ dependence of θ) [17]. The presence of some organic molecules may in some cases be detected even at a level of 10^{-8} M by means of a perfectly clean and active noble metal surface and this should be remembered when evaluating the reliability of the redox potential measurements in strongly organic contaminated environments.

IJzermans also gave evidence of this effect of H_2S at the platinum electrode by potentiodynamic experiments. With the bright platinum electrode, starting from the NHE potential, at +50 mV the anodic process



begins. Up to 300 mV the current remains higher for the H_2S -free than for the H_2S -saturated solutions, as the H adsorption is weaker and the process faster, going rapidly to completion, forms a surface clean and active up to approx. 900 mV where another anodic reaction starts. In H_2S -saturated solutions the ionization of the adsorbed H atoms is followed by the formation of a poisoning S layer and the current after 500 mV

rapidly increases. The presence of such a layer accounts for the lower currents (with respect to the H_2S -free solutions) after the inversion of the potential cycle. The curves are instructive also because they show the range of potential at which platinum can be kept free and active in strongly acidic solutions (H_2SO_4 0.5 M) and in the absence of H_2S .

So, in the presence of H_2S the conditions for assuring a free and active platinum surface are determined first by the thermodynamic conditions of coexistence of the metal with its monosulphide, the corresponding potential being given by the relationship:

$$E \text{ (mV)} = \frac{10.2 \cdot 1000}{2 \cdot 23.06} - 59.1 \cdot \text{pH} + 29.5 \log_{10} \text{pH}_{25} \quad (1)$$

(10.2 being the standard molar free energy (in Kcal) involved in the sulphurization reaction) and second, by the kinetic parameters governing the chemisorption process. In any case one should be aware of the possibility that the electrical potential may be shifted in the direction of the lower value corresponding to that of the adsorbed atomic hydrogen. The presence of oxygen can improve the situation as it acts as a hydrogen acceptor.

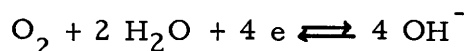
Let us now consider the limitation to the applicability of platinum as a redox electrode at more positive potentials. In acidic solutions ($\text{pH} \sim 0$) at about 900 mV vs. NHE, a monomolecular layer of oxygen forms over the metal surface. At this point the process is still reversible and the conductivity of this layer allows the exchange of electrons. As the potential increases the anodic process becomes irreversible with penetration of oxygen atoms into the metal lattice (dermasorbed layer). At 1200 mV and more, more or less hydrated and oxygenated platinum oxide phases are built up on the surface. They show lower conductivity and do not allow sufficient exchange current densities for the redox processes (especially at low concentrations) to keep the potential at the true redox value. The electrode then assumes a potential shifted towards that of an oxide electrode, to a degree depending on the thickness of the oxide layer and the smallness of the redox component concentrations.

From the above considerations we can conclude that the upper limit of use of a platinum electrode as redox sensor should be cautiously put at about 1000 mV in strongly acidic solutions, i. e. about 600 mV at pH 7 vs. NHE (approx. 360 mV at pH 7 vs. saturated calomel electrode). The lower limit, from a thermodynamic point of view, is determined by the relationship (1) which gives a value of -193 mV (NHE -434 mV vs. SCE) at pH 7 for H_2S -saturated solutions at 25°C . Other limitations, however, may arise from the kinetics of the adsorption processes. For these pro-

cesses it should be remembered that the layer of the chemisorbate can be easily removed and the surface restored, by a suitable anodic cleaning at potentials lower than those corresponding to the other irreversible anodic processes.

Polarization Phenomena

The analysis of the contributions to the total electrode overvoltage due to the space charge and to the chemical reactions involving the dissolved species is complicated by their mutual interactions and is outside the scope of this discussion. The overvoltage contribution due to diffusion and transport processes, is, however, formally more simple when they represent the rate determining steps of the overall electrode reaction. So it seems to us worthwhile to warn against the remarkable errors that can be made during the E_h measurements when a finite transport process takes place in the vicinity of the electrode surface, as happens when the input impedance of the measuring electrometer is not very high. We assume as first approximation (more valid the more dilute the solution) that the principle of independent migration applies, i. e. the diffusion of the electroactive species is independent of the concentration of the other dissolved species. Let us consider, as example, the electro-chemical reaction:



and in particular the process of diffusion of molecular oxygen, whose driving force is the appropriate thermodynamic activity gradient.

In stationary conditions the activity at any value of the spatial coordinate (distance from the electrode-electrolyte interface) is obtained by equating to zero the terms containing the partial derivatives with respect to time in Fick's equation. By integrating and introducing the nernstian formalism of the limiting diffusion layer, we obtain for the flux of oxygen through the layer:

$$\phi_{O_2} = \frac{\bar{D}_{O_2}}{\delta} (a_{O_2} - a_{O_2}^*)$$

\bar{D}_{O_2} being the average diffusion coefficient in the diffusion layer δ , a_{O_2} and $a_{O_2}^*$ the oxygen activities at the external boundary of δ and at the interface with the electrode, respectively. If J is the current density and F the Faraday constant, this yields:

$$J = 4 F \phi_{O_2}$$

and

$$a_{O_2}^* = a_{O_2} - \frac{J}{K}$$

where:

$$K = \frac{4 F \bar{D}_{O_2}}{\delta}$$

The basic Nernst relationship for the electrode potential gives:

$$E = E^{\circ} + \frac{RT}{4F} \ln \left[a_{O_2} / a_{OH^-} \right]$$

and

$$E^* = E^{\circ} + \frac{RT}{4F} \ln \left[a_{O_2}^* / a_{OH^-} \right]$$

where E° is the normal potential of the redox couple. The diffusion overvoltage is then given by:

$$\eta_d = E^* - E = - \frac{RT}{4F} \ln \left[\frac{K \cdot a_{O_2}}{K \cdot a_{O_2} - J} \right]$$

For $J \neq 0$, η_d vanishes only when $K \rightarrow \infty$, i. e. for $\delta = 0$. The factor which has greatest influence on the value of δ is the state of turbulence of the solution; as the more the solution is stirred, the lower is δ and thus η_d .

We stated these well-known fundamental concepts in order to correlate them with the situation of measurements of the redox potential distribution through the depth of a mud layer. In this case, not only any possibility of mechanical stirring is precluded, but the concept of δ is poorly defined. In fact, the vicinity of the electrode surface in which the diffusion layer is usually defined, is now occupied by the solid particles and many of them are in contact with the electrode. So, the configuration of the macroscopic system consisting of the electrode, liquid and sedimentary phases depends on many geometrical factors (granulometry, packing factor of the sediments, etc.) and consequently a diffusion layer is not defined. For this reason the adoption of a measuring circuit having an extremely high impedance is imperative.

Perturbation Transients

Let us, as a preliminary, say that in basins which are not highly polluted the most important primary redox process is the reaction between water and oxygen, in equilibrium with hydroxyl ions; of paramount importance is the chemical interchange between air and water which strongly affects the other redox equilibria, thus varying the rates between the concentrations of the oxidized and reduced species of each individual redox couple. The molecular oxygen migrates by both diffusion and stirring depending on climatological events from the surface towards the se-

diments. Since oxygen takes part in almost all processes of chemical and biological decomposition of the settled, dead planctonic species, its rate of migration affects the kinetics of these processes; to such a degree that, under conditions of prolonged calm, in certain basins the oxygen transport may prove the limiting factor for these degradative reactions (note 1).

Their kinetics, of course, are not constant at different depths of the sedimentary layer. If we ideally slice the layer in many horizontal thin sublayers, as we proceed from the upper towards the older, deeper sublayers, we expect a slackening of the chemio- and bio-degradation kinetics, because of both the continuously decreasing concentration of the residual degradable matter and the continuously decreasing concentration of oxygen, which reaches the sublayer surviving the processes occurring in the upper ones.

Therefore, with any defined hydrodynamic condition, there is at any depth a corresponding determined set of concentrations of reactants and products of each individual reaction. A dynamical equilibrium is then established which depends on the rate of diffusion of oxygen, reactants and products of any single process as well as on the rate constants of all the processes. So, with any defined hydrodynamic condition is associated a stationary state of the system and a set of well defined ratios of the oxidized and reduced form of any individual redox couple. The redox potential and its gradient as a function of depth represent the electrochemical image of this stationary condition as far as the degree of oxidation is concerned.

If a perturbation is now introduced, the redox potential and its gradient become functions of spatiotemporal parameters, even after the perturbation has ceased. The equations describing such parameters are extremely complex and practically insoluble.

Unfortunately, when measuring the redox potential in the sediments, mechanical perturbations cannot be avoided because it is not possible to avoid one sampling operation and the transfer of the sample on the ground. Particularly, in the sampling operation, however much care is taken, a certain mechanical disturbance is unavoidable. By making use of the standard Jenkins apparatus and technique, however, a blending of the par-

(note 1) In the absence of oxygen other biochemical transformations may take place when sufficient concentrations of nitrogen, sulphur or carbon are present, yielding ammonia, hydrogen sulphide and methane, respectively. The processes involving these hydrogen acceptors are always alternative with respect to those involving oxygen, as they are due to the presence of anaerobic species.

ticles lying at different depths is minimized, so that the above mentioned sublayers, after the initial mechanical shock, resettle in their original distribution; the same happens after a very careful dipping of the redox electrode system into the mud layer.

EVALUATION OF THE STEADY STATE E_h DISTRIBUTION AT DIFFERENT DEPTHS

The above mentioned sublayer rearrangement in the original distribution would theoretically take an infinite time, so that, from this point of view a long wait between sampling and E_h measurements would be suitable. But, on the other hand, too long a waiting time may result in alterations of the original situation. Let us examine one cause of alteration connected with the exigencies of the measurements themselves.

During the whole operation it is never possible to exclude air from the water column overlaying the sediments as a temporary contact, at least when the electrode system is dipped in, is unavoidable; so it is not possible to assume that the oxygen concentration at the top of the water column maintains its original value after the electrode introduction. As a consequence, the oxygen transport process towards the mud layer undergoes an alteration with respect to the "in field" conditions. Apart from any other mechanical perturbation, when the perturbation introduced with the air contact reaches the sediments it induces a corresponding, progressive variation of the oxygenation conditions in the mud. From this other point of view E_h should be measured as soon as possible after the sampling.

From the foregoing, it should be easy to draw the conclusion that there should be a certain length of time after sampling at which a minimum departure of the measured values from the "true", in field values, takes place. Concerning this problem Mortimer [18] estimated that a waiting time of two or more hours is needed in order to minimize the effects of the electrode introduction, this being the only cause of perturbation he took into account. Nevertheless, this seems to be an oversimplified treatment of this important problem, as the optimum time value must depend on many parameters, namely the time of resettling of the mud layer in its original position, the particle size and the particle size distribution, the density of the particles, the extent of water aeration before rebunging after the electrode introduction, the height of the water column above the mud layer and so on, so that an "a priori" fixing of the best waiting time after sampling and electrode introduction seems impossible to assess.

In theory, the only way to solve the problem apparently lies in the possibility of discriminating between the two concurrent processes of layers resettling and of oxygen transport; this seems possible only if the rate

of the process of oxygen migration through the water column overlaying the sediments is large as compared with the rate of rearrangement of the sublayers after the electrode introduction. Obviously, a skilful sampling, an unshaken transfer of the column in the laboratory, a cautious introduction of the electrodes as well as the absence of vibrations during the measurements increase the difference of the rate constants of the two processes, so improving the possibility of discrimination.

By analyzing the evolution with time of the measured E_h values we expect to display the two effects, especially when measurements are carried out at the same time at different depths with a multiple redox electrode in reducing muds. In this case, when an appreciable amount of the oxygen passed through the water progressively reaches the individual redox electrodes, a faster increase (or a slower decrease) of the corresponding E_h evolution versus time would take place.

We propose cutting the curve at this point (i. e. neglecting the successively measured E_h values), extrapolating the values measured with an analytical function showing a horizontal asymptote and to take the asymptotic value for each electrode as the stationary E_h value corresponding to the steady state hydrodynamic condition at the moment of the sampling and with the oxygen transport perturbation excluded.

Experiments

In order to support the previous considerations and to test the validity of our proposal, we performed some determinations of E_h profiles at different depths in Lake Lugano sediments. This mud, especially in summer, is strongly reducing, so that negative values of E_h are to be expected. This fact provides the best conditions for evaluating the spurious effects of oxygen transport.

Surface sediment cores were collected with a Jenkin sampler during a stratification period in 1973. Sampling depths varied from a minimum of 50 m (Ponte Tresa) to a maximum of 310 m (Gandria). The chemical characteristics of Lake Lugano sediments have been reported in another paper [19].

Particular care was devoted to preserving an intact mud-water interface, discarding those cores showing some turbidity in the water column. The core must not retain any air at its top and immediately after sampling it was transferred with the utmost care on land. Soon afterwards each core was then carefully opened and the bung replaced by another one carrying the platinum electrode sheaf as well as the reference electrode. Before plugging, both the temperature and the pH values were taken.

Redox measurements were carried out with a modified Mortimer's multiple electrode. The sheaf with the electrodes placed at eight pre-set distances was carefully dipped into the sediment avoiding mechanical disturbances as far as possible. The electrode depths in the core (water + sediment) were: +50, +10, interface, -5, -10, -20, -30 and -50 mm.

A saturated calomel electrode was employed as a standard reference. The electrode circuit was put in opposition with a bridge and a Keithley Electrometer Mod. 601 was employed as a zero current (input impedance $> 10^{14}$ Ohm), zero point, millivoltmeter. More details have been reported in a previous paper [20].

The measurements started generally half an hour after sampling. Fig. 1 shows a typical long-time evolution of E_h values; it is possible to notice that the E_h values measured in the sediment decrease with time up to 200 min and afterwards they increase.

On the contrary, the electrodes placed 10 and 50 mm above the mud-water interface give stable values up to 300 min. From this it is possible to infer that the effects of the disturbances pertaining to the sampling and to the electrode introduction disappear at a much quicker rate than those due to the oxygen transport from the top of the column towards the mud-water interface.

From Fig. 2 it is possible to observe that the E_h values in the vicinity of the interface (e.g. -5, -10 mm) are sometimes more negative than those corresponding to deeper layers. This should not be completely unexpected as it may be accounted for by an abnormal fall-out and accumulation of the bio- and the chemi-degradable mass. When this happens, the oxygen-demanding reactions may take place at a rate so fast as to leave local strongly reducing conditions.

In most cases the trends of the curves suggest that they can be represented by branches of equilateral hyperbolae with horizontal asymptotes.

A least squares Fortran program was developed to obtain a best fit to the experimental results and to find the individual asymptotic values. These values were subsequently corrected to pH 7 and plotted against the height, down and above the mud-water interface (Fig. 3).

DISCUSSION AND CONCLUSIONS

We have, so far, described the main foreseeable causes of perturbation and errors which occur in the experimental determination of the redox potential profiles in the sediments at different depths. This does not mean,

that other causes of perturbation should be excluded under some circumstances.

First of all, some movements of particles and of interstitial water may occur in the vicinity of the individual redox electrodes. Such movements may be accounted for by the presence of living species (benthos, etc.) and the evolution of gases resulting from bottom putrefactive processes.

The latter phenomena take place when, owing to lack of oxygen, sulphur, or carbon, or both, become hydrogen acceptors evolving hydrogen sulphide and methane under the action of anaerobic micro-organisms. In particular, the evolution of hydrogen sulphide may be very large in correspondence to high concentrations of sulphate ions; as the gas reaches the aerobic zones even out of the sedimentary layer, it may undergo an oxidation to elemental sulphur which falls down together with the dead planctonic species [12].

The normal potential of the couple sulphur ions-sulphur is somewhat negative so that an eventual attack of platinum in these conditions should be accompanied by a displacement of the electrode potentials towards very negative values. Apparently, also because of the extremely low equilibrium S-concentration in non alkaline conditions, the reaction rate is very low. Hayes and coworkers [11] observed the formation of an amber tarnishing layer after many hours of Pt electrode immersion in a sulphide rich mud. After our experiments we did not observe any visible alteration of the platinum electrode surfaces.

As far as our fundamental assumption that the measured redox potential values, extrapolated to infinite time, are close to the "true" in-field values is concerned, we are perfectly conscious that it is open to criticism. As a matter of fact, a direct demonstration is not possible owing to the dishomogeneities of the mud layer; moreover, even if it were possible to exclude the whole mud sample rigorously from any contact with air during the electrode introduction, it is never possible to assume the invariance (with respect to the in-field conditions) of the hydrodynamic conditions and the phenomena occurring in the overlaying water (oxygen diffusion, plancton sedimentation, natural displacements of the overlaying water layers, etc.).

In our sample containers the rates of all these phenomena are negligibly small, thus reproducing conditions of stillness. Evidently, in the case of sediments in contact with fast moving waters (such as, for instance, rivers) our assumption is no longer valid. On the other hand, in stagnant or quasi stagnant waters the method of cutting out the long-time measured E_h values and of extrapolating the short-time values to infinite time, seems to be the

only way of eliminating the perturbation effects of the sampling and of the electrode introduction.

This procedure should probably be capable of extension to the determination of the profiles of other electrochemical quantities in the sediment layers.

ACKNOWLEDGEMENTS

The authors wish to thank Professor S. Trasatti (Institute of Electrochemistry, University of Milan) for a helpful discussion and Mr. B. Dorpema for the development of the Fortran-IV computer program.

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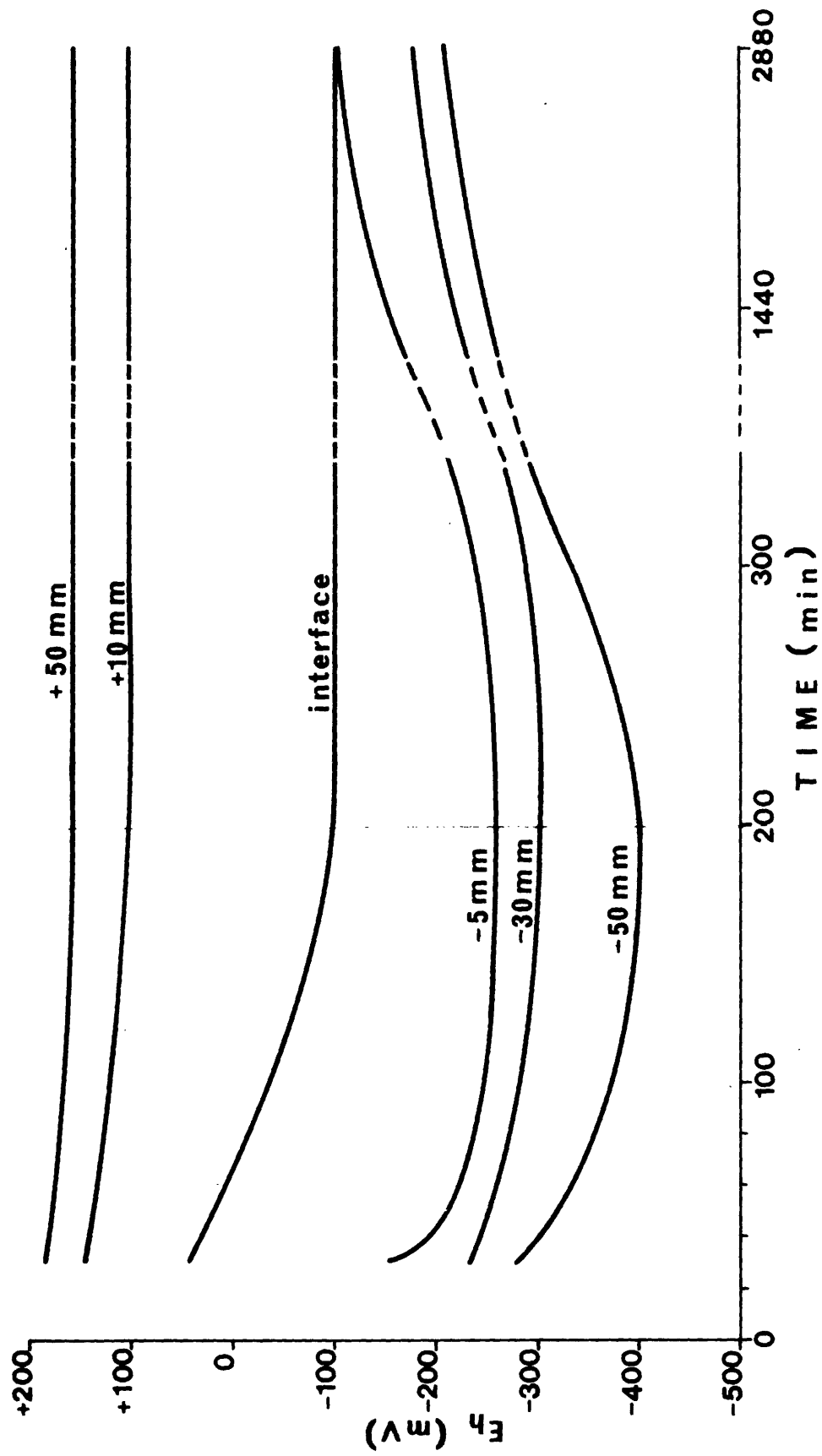


Fig.1_ Time variation of E_h values at different depths in a core collected from Lake Lugano (Melide, May '73).

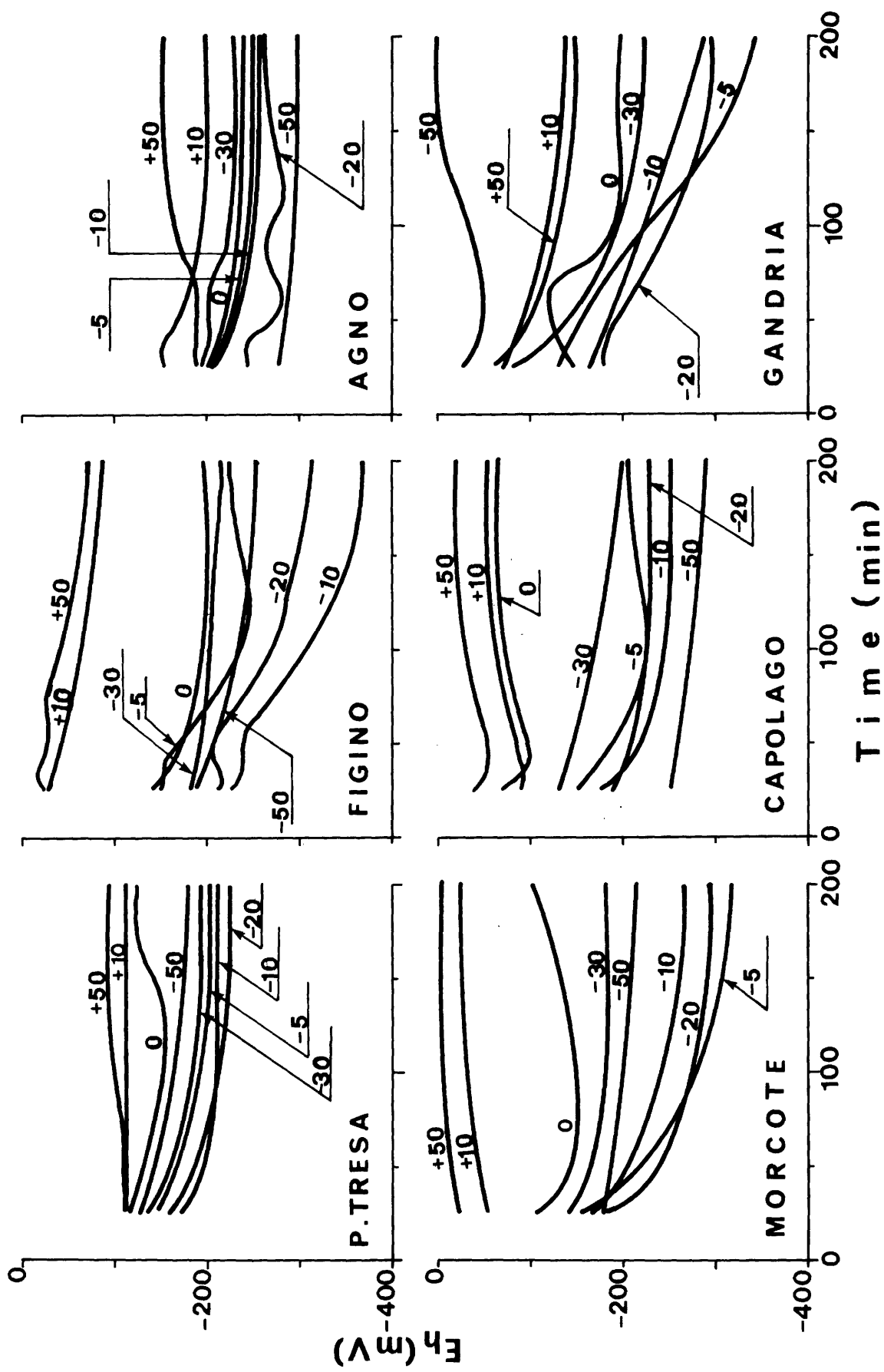


Fig.2_Effect of time on potential readings at various mud depths (mm).

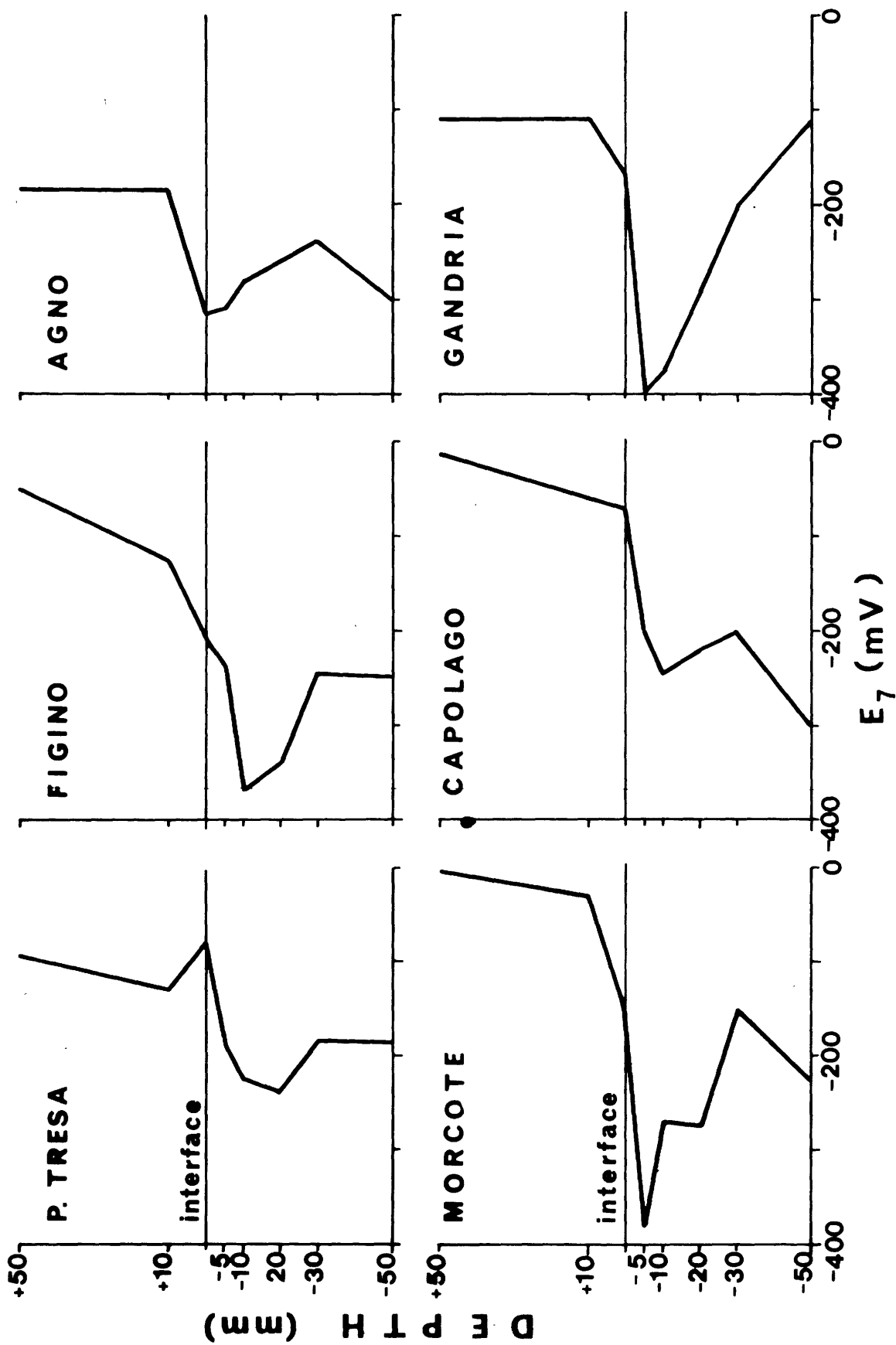


Fig.3-The redox potential at various core depths in Lake Lugano.

European Communities — Commission

EUR 6035 — Reliability conditions of E_h measurements in lake sediments

G.B. Barbi, G. Premazzi, Joint Research Centre, Ispra Establishment, Italy

Luxembourg : Office for Official Publications of the European Communities

1978 — 20 pp. — 21.0 x 29.7 cm

Environment and quality of life series

EN

ISBN 92-825-0681-9

Catalogue number : CD-NO-78-017-EN-C

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The main possible causes of perturbation in the determination of redox potential profiles in lacustrine sediments have been examined in detail. They are :

- (1) electrochemical, consisting both in the possibility of surface alterations due to chemical processes, and in the electrode polarization in non-electrometric conditions of measurement;
- (2) due to the sampling operation and, more generally, to transient alterations of the original layer distribution.

As far as the first point is concerned, the possibility of the formation of a non-metallic superficial phase containing either S or O_2 on the bright platinum electrode, has been evaluated from a thermodynamical point of view. The upper and lower limits of the electrode potential for which platinum can be used as a redox electrode, was also determined.

As to the second point, an experimental methodology and the use of a suitable computational programme have been developed. They allow the cutting off of the spurious contributions due both to the morphological perturbations of the mud layers because of the sampling and introduction of the polyelectrode, and to those due to the oxygen transport process towards the mud-water interface.

Such methodology has a quite general character and has been successfully applied to the determination of the redox potential profiles in Lake Lugano; extension to the evaluation of the profiles of other chemical and electrochemical quantities in the sedimentary layers is planned.